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Controlling the Sulfur Poisoning of Ag/Al₂O₃ Catalysts for the Hydrocarbon SCR Reaction by Using a Regenerable SO_x Trap.

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Abstract

The deactivation of a silver-based hydrocarbon selective catalytic reduction catalyst by SO_x and the subsequent regeneration under various operating conditions has been investigated. Using a sulfur trap based on a silica-supported catalyst it was found that, for a Ag/SiO₂ + Ag/Al₂O₃ combination, the negative effect of SO₂ on the *n*-octane-SCR reaction can be eliminated under normal operating conditions. The trap can be regenerated by hydrogen at low temperatures or at higher temperatures using a hydrocarbon reductant.

Keywords: Ag catalysts, NO_x reduction, SO_x trap, *n*-octane, HC-SCR, Regeneration

Introduction

Lean-burn diesel engines offer significant fuel efficiency advantages as compared with stoichiometric gasoline engines. However, in diesel engines nitrogen oxides (NO_x) are produced in the presence of a large excess of oxygen. This creates a problem for the *reduction* of NO_x under *oxidising* conditions, causing air pollution. One of the promising approaches to eliminate NO_x is to use the selective catalytic reduction (SCR) with hydrocarbons (HC-SCR) using silver-based catalysts [1-24]. It is well-known, however, that sulphur oxides (SO_x) are detrimental to the HC-SCR activity on Ag catalysts at temperatures between about 300 and 500 °C [5, 11-24].

Recent research by Li and King [25] has shown that SO_2 can be efficiently trapped on Ag/SiO₂ catalysts over a wide range of temperatures (300 – 550 °C) under lean conditions. Moreover, these materials can be completely regenerated by a CO/CO₂/C₃H₆/H₂ mixture during rich cycles at the same temperature. This is very interesting because Ag/Al₂O₃ deactivated by SO_x can also be regenerated under rich conditions at high temperatures [5, 13, 17, 18]. Therefore, the use of Ag/SiO₂ as a SO_x absorbent upstream of Ag/Al₂O₃ during the HC-SCR reaction at intermediate temperatures (i.e. ca. 300 – 500 °C) could be a practical way to protect the HC-SCR catalyst. In this study, we have investigated the efficacy of SO_x trapping and regeneration (RG) on HC-SCR activity using a double bed system. In addition, we have investigated appropriate regeneration conditions needed to reactivate any deactivated Ag catalysts.

2. Experimental

2.1 Catalyst Preparation

The Ag/Al₂O₃ catalyst, obtained from Johnson Matthey plc, was prepared by impregnation of γ -Al₂O₃ (LaRoche Industries Inc.). The Al₂O₃ support material was ground to a particle size of < 250 μm and mixed with a solution containing 0.022 M AgNO₃. The catalyst was then filtered, dried at room temperature for 24 h and further dried at 100 °C for 3 h, after which the catalyst was calcined at 550 °C for 3 h [10]. For the preparation of the SO_x trap material the Ag/SiO₂ catalyst was prepared by incipient wetness impregnation of the SiO₂ support using AgNO₃. The resulting catalyst was then dried at 100 °C overnight and then calcined at 550 °C for 4 h. Although Li and King [25] have reported that there is no significant effect of Ag loadings between 2.5 and 10% on SO_x trap performance, 5% Ag loading show the highest performance. Therefore, 5% wt of Ag/SiO₂ was used in this study. The Ag content of the catalyst was determined by the Direct Current Plasma method to be approximately 2 wt% and 5 wt% Ag, and the BET specific surface areas of the catalysts were 170 m² g⁻¹ and 293 m² g⁻¹ for Ag/Al₂O₃ and Ag/SiO₂, respectively.

2.2 SO₂ deactivation, trap and regeneration

The catalytic performance of both Ag catalysts was measured in a fixed-bed flow reactor system consisting of a quartz reactor tube. The catalysts were held in place between plugs of quartz wool and a K-type thermocouple was placed in the centre of each catalyst bed. Single and dual catalyst beds with separate furnaces were used in this study. The 5% Ag/SiO₂ catalyst was placed upstream of the 2% Ag/Al₂O₃ catalyst. The gap between both Ag beds was ca. 50 cm. Each of the gases in the feed system was controlled individually by mass flow controllers, while *n*-octane and water vapour were introduced to the system by means of separate saturators with Ar as a

carrier gas. The n -C₈H₁₈ saturator was placed in an ice/water bath where its temperature was carefully controlled while the temperature of the H₂O saturator was controlled using a thermostatic bath. All the lines following the water saturator were heated to prevent condensation. The feed gas stream consisted of NO, C₈H₁₈, O₂, H₂O, CO₂, H₂, SO₂ and Ar balance. The total gas flow rate was 276 cm³ min⁻¹ over 276 mg of each Ag catalyst which was sieved to obtain particle sizes between 250 and 450 µm. The inlet and outlet NO_x concentrations were determined by a Signal 4000VM series chemiluminescence detector. In these studies, total NO_x conversion is defined as NO_x reduction to N₂ and N₂O.

Several different gas mixes were used as follows.

GM₁: 720 ppm NO; 4340 ppm (as C1) C₈H₁₈; 4.3% O₂; 7.2% CO₂; 7.2% H₂O

GM₂: 720 ppm NO; 4340 ppm (as C1) C₈H₁₈; 4.3% O₂; 7.2% CO₂; 7.2% H₂O; **1-30 ppm SO₂**

RGM₁: 720 ppm NO; 4340 ppm (as C1) C₈H₁₈; 7.2% CO₂; 7.2% H₂O; **1-30 ppm SO₂; 2% H₂**

RGM₂: 720 ppm NO; 4340 ppm (as C1) C₈H₁₈; 7.2% CO₂; 7.2% H₂O; **1-30 ppm SO₂; 16000 ppm C₈H₁₈ (as C1)**

RGM₃: 720 ppm NO; 4340 ppm (as C1) C₈H₁₈; 7.2% CO₂; 7.2% H₂O; **0.5% O₂; 1-30 ppm SO₂; 16000 ppm C₈H₁₈ (as C1)**

The SCR activity of the Ag catalysts was investigated as a function of time on stream at 350 °C without the presence of SO₂ (using gas mixture GM₁) for 15 h in order to obtain the baseline of NO_x conversion. SO₂ was then added to the SCR gas mix (GM₂) with different concentrations of SO₂ for 15 h to examine whether or not deactivation had taken place for both single Ag/Al₂O₃ and dual Ag/SiO₂ and Ag/Al₂O₃ catalyst beds. In order to prevent a saturation of adsorbed SO_x on the Ag catalysts, the regeneration process was carried out at 550, 600 or 650 °C for 1 or 5 min under different regeneration mixes using the procedure outlined in Figure 1. NO_x conversions were measured at 350 °C under GM₂ after 3 h of each regeneration step when using 30 ppm SO₂ and after 6 h when using 1, 5 or 10 ppm SO₂ in the SCR feed.

2.3 Temperature-programmed reaction (TPR)

The SO₂-TPR experiments were carried out to investigate the desorption properties of adsorbed SO_x on 5% Ag/SiO₂. Prior to the measurements, 276 mg of 5% Ag/SiO₂ catalyst was exposed to GM₂ consisting of 720 ppm NO, 4340 ppm (as C1) C₈H₁₈, 4.3% O₂, 7.2% CO₂, 7.2% H₂O, 10 ppm SO₂ and Ar balance at 350 °C for 6 h. The total flow rate was 276 cm³ min⁻¹. The resulting Ag catalyst was then used for SO₂-TPR measurements. Approximately 50 mg of SO₂-pretreated Ag/SiO₂ catalyst was exposed to different gas regeneration mixes (RGM_x without SO₂) with a total flow rate of 100 cm³ min⁻¹ for 15 min at 100 °C before increasing the temperature up to 750 °C at a rate of 10 °C/min. Desorbed H₂S, COS and SO₂ species were monitored by a Hiden Analytical HPR20 quadrupole mass spectrometer.

3. Results and Discussion

3.1 The effect of SO₂

Figure 2 shows the effect of exposure to SO_2 on the $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst under SCR gas mix (GM_2) containing 5 ppm SO_2 for a period of 15 h at different temperatures. It is clearly seen that only a very small amount of deactivation was observed at 550 °C after 15 h with 5 ppm SO_2 in the SCR gas mix. However, at any of the lower temperatures tested, there was severe deactivation over a period of 6-15 h with the NO_x conversion decreasing to zero. Please note that the catalytic activity tests under SCR gas mix (GM_1) were also performed over Ag/SiO_2 on its own and NO_x conversions of ca. 1% (not shown) were observed at 300 and 350 °C. This is consistent with the research work by Bethke and Kung [26] that Ag/SiO_2 has very poor SCR activity with propene at 400 °C (8% NO conversion to only N_2O).

To investigate the effect of the SO_2 trap, both single $\text{Ag}/\text{Al}_2\text{O}_3$ and dual Ag/SiO_2 and $\text{Ag}/\text{Al}_2\text{O}_3$ catalysts were exposed to the SCR gas mix with and without SO_2 as shown in Figure 3. Prior to the addition of SO_2 into the SCR feed, the catalytic activity (Fig. 3a, dashed line) was very stable and there was no deactivation observed over 15 h. However, there is a small decrease in NO_x conversion from 89 to 67% when adding 1 ppm SO_2 into the SCR gas mix. Figure 3a also shows the negative effect of SO_2 on the SCR activity of the $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst, which deactivated significantly when exposed to 5, 10 or 30 ppm SO_2 over the course of experiments at 350 °C, showing decrease in NO_x conversions from ca. 90 to 0%. Although the fact that deactivation of $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst by SO_2 was reported in many papers, the deactivated catalysts could not easily be regenerated [5, 13, 17, 18].

It is, therefore, very interesting to see the effect of using the SO_x trap to protect the $\text{Ag}/\text{Al}_2\text{O}_3$ bed when this was tested using an octane-SCR mixture (GM_2). Of course, without a regeneration process, saturation of the Ag/SiO_2 catalyst will eventually result in deactivation of the $\text{Ag}/\text{Al}_2\text{O}_3$. Figure 3(b) shows that this only occurs after about 6 h on stream when using 10 ppm of SO_2 which can be compared with much less than 1 h without the SO_x trap in place.

3.2 The effect of regeneration

Prior to the saturation of Ag/SiO_2 by adsorbed SO_x the effect of regeneration was investigated by exposing both Ag/SiO_2 and $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst beds to different regeneration gas mixes at three different temperatures. Note that above 550 °C the deactivation of $\text{Ag}/\text{Al}_2\text{O}_3$ by SO_2 does not occur (Figure 2).

Figure 4 shows the profiles of SO₂ released into the gas phase during temperature-programmed reduction under different gas mixes. Note that no H₂S and COS was observed to be released from the Ag/SiO₂ catalysts (not shown). Using gas mixture RGM₁ containing hydrogen we observe a remarkable regeneration of the Ag/SiO₂ at temperatures between 200 and 400 °C which can be contrasted with the profile obtained using a 5% O₂/Ar feed. Figure 4 also shows that the octane in the absence of hydrogen is much less effective at regenerating the Ag/SiO₂ SO_x trap. This is consistent with the literature [5, 17, 18, 25] which reports that heating in the presence of H₂ could almost fully regenerate deactivated Ag catalysts. The effect of the most favourable regeneration conditions (RGM₁) is shown in Figure 5. For both single Ag/Al₂O₃ and dual Ag/SiO₂ + Ag/Al₂O₃ beds, the initial NO_x conversion on fresh samples over a period of 15 h under gas mixture GM₁ was ca. 89%. In the absence of the Ag/SiO₂ trap, as expected, deactivation of the Ag/Al₂O₃ catalyst is severe (Please note that SO₂ was never removed from the feed once introduced into the SCR gas mix). After 1 min regeneration under RGM₁ at 550 °C, the SCR activity observed over a period of 6 h under GM₂ was very poor. On the other hand, when using Ag/SiO₂ upstream as a SO_x trap, there was very little deactivation. The decrease in NO_x conversion was only 2% over the course of 48 h. The SCR activity on the downstream Ag/Al₂O₃ after the third time of regeneration was equally high, giving a NO_x conversion of ca. 87%.

The effect of regeneration was probed using RGM₁ containing small amount of octane and 2% H₂ at 550 °C for 1 and 5 min. Figure 6 compares the effect exposure to different concentrations of SO₂. For 1 or 5 ppm, it was found that, as expected, the regeneration is very high even after a total exposure of 27 h before the third regeneration. NO_x conversions in both cases were maintained above 85%. In contrast, at the very high concentrations of 10 or 30 ppm of SO₂ the trapping by the Ag/SiO₂ is not complete and progressive deactivation of the Ag/Al₂O₃ occurs. However, for a normal low sulphur diesel fuel, with a sulphur level below 10 ppm, the concentration of SO₂ in the exhaust would be < 1 ppm and the results in Figure 6 show that, under those conditions, we can achieve excellent protection of the silver HC-SCR catalyst.

Figure 7 compares the different regeneration mixtures, with or without hydrogen and at different temperatures. Overall, although the presence of hydrogen is very favourable, good regeneration can be achieved in the absence of hydrogen by using higher temperatures and/or longer regeneration times.

Conclusions

SO₂ deactivation and regeneration has been investigated over dual Ag/SiO₂ + Ag/Al₂O₃ catalytic systems. It was found that the negative effect of SO₂ on the *n*-octane-SCR of NO_x reaction over a Ag/Al₂O₃ catalyst can be almost eliminated when using Ag/SiO₂ as a SO_x trap material.

Acknowledgements

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References

- [1] Breen JP, Burch R (2006) Top Catal 39:53

- [2] Breen JP, Burch R, Hardacre C, Hill CJ, Rioche C (2007) J Catal 246:1
- [3] Burch R, Breen JP, Hill CJ, Krutzsch B, Konrad B, Jobson E, Cider L, Eränen K, Klingstedt F, Lindfors LE (2004) Top Catal 30-31:19
- [4] Burch R, Breen JP, Meunier FC (2002) Appl Catal 39:283
- [5] Breen JP, Burch R, Hardacre C, Hill CJ, Krutzsch B, Bandl-Konrad B, Jobson E, Cider L, Blakeman PG, Peace LJ, Twigg MV, Preis M, Gottschling M (2007) Appl Catal B 70:36
- [6] Bentrup U, Richter M, Fricke R (2005) Appl Catal B 55:213
- [7] Eränen K, Klingstedt F, Arve K, Lindfors LE, Murzin DY (2004) J Catal 227:328
- [8] Shimizu K, Satsuma A (2006) Phys Chem Chem Phys 8:2677.
- [9] Satokawa S, Shibata J, Shimizu K, Atsushi S, Hattori T (2003) Appl Catal 42:179
- [10] Eränen K, Lindfors LE, Niemi A, Elfving P, Cider L (2000) SAE Paper 2000-01-2813
- [11] Nakatsuji T, Yasukawa R, Tabata K, Ueda K, Niwa M (1998) Appl Catal B 17:333
- [12] Houel V, James D, Millington P, Pollington S, Poulston S, Rajaram R, Torbati R (2005) J Catal 230:150
- [13] Houel V, Millington P, Pollington S, Poulston S, Rajaram R, Tsolakis R (2006) Catal Today 114:334
- [14] Meunier FC, Ross JRH (2000) Appl Catal B 24:23
- [15] Meunier FC, Zuzaniuk V, Breen JP, Olsson M, Ross JRH (2000) Catal Today 59:287
- [16] Meunier FC, Ukropec R, Stapleton C, Ross JRH (2001) Appl Catal B 30:163
- [17] Shimizu KI, Higashimata T, Tsuzuki M, Satsuma A (2006) J Catal 239:117
- [18] Shimizu KI, Tsuzuki M, Satsuma A (2007) Appl Catal B 71:80
- [19] Sumiya S, Saito M, He H, Feng QC, Takezawa N, Yoshida K (1998) Catal Lett 50:87
- [20] Abe A, Aoyama N, Sumiya S, Kakuta N, Yoshida K (1998) Catal Lett 51:5
- [21] A. Keshavaraja A, She X, Flytzani-Stephanopolous M (2000) Appl Catal B 27:L1
- [22] Jen HW (1998) Catal Today 42:37
- [23] Angelidis TN, Kruse N (2001) Appl Catal B 34:201
- [24] Angelidis TN, Christoforou S, Bongiovanni A, Kruse N (2002) Appl Catal B 39:197
- [25] Li L, King DL (2010) Appl Catal B 100:238
- [26] Bethke KA, Kung HH (1997) J Catal 172:93

Figures and Captions

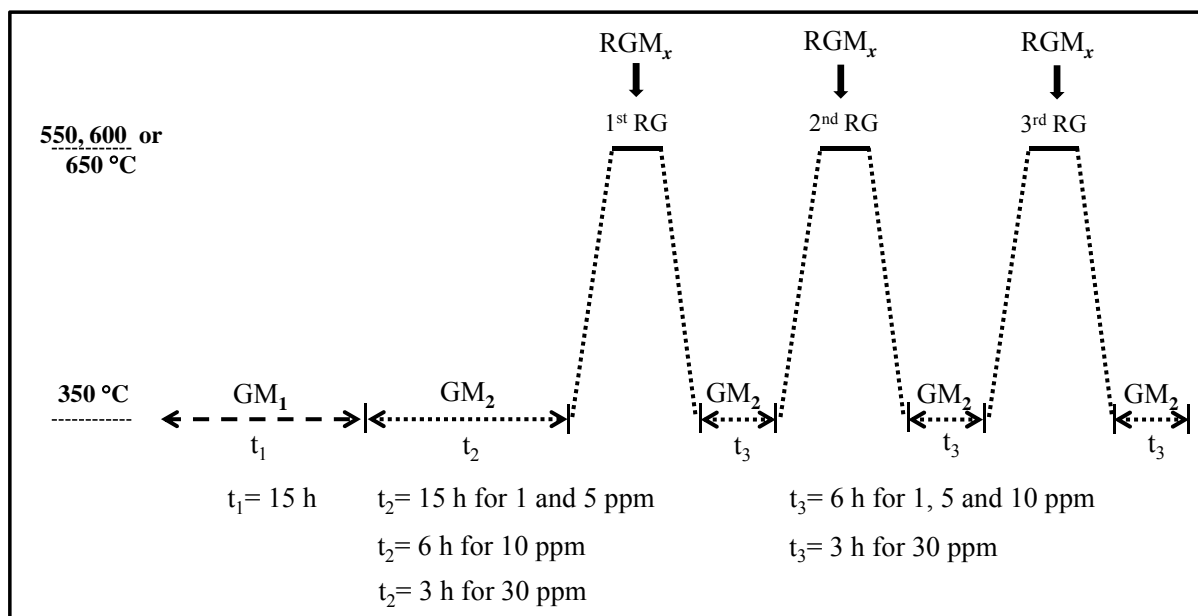


Figure 1 Experimental protocols for the regeneration of 5% Ag/SiO₂ and 2% Ag/Al₂O₃ during octane-SCR of NO_x at 350 °C.

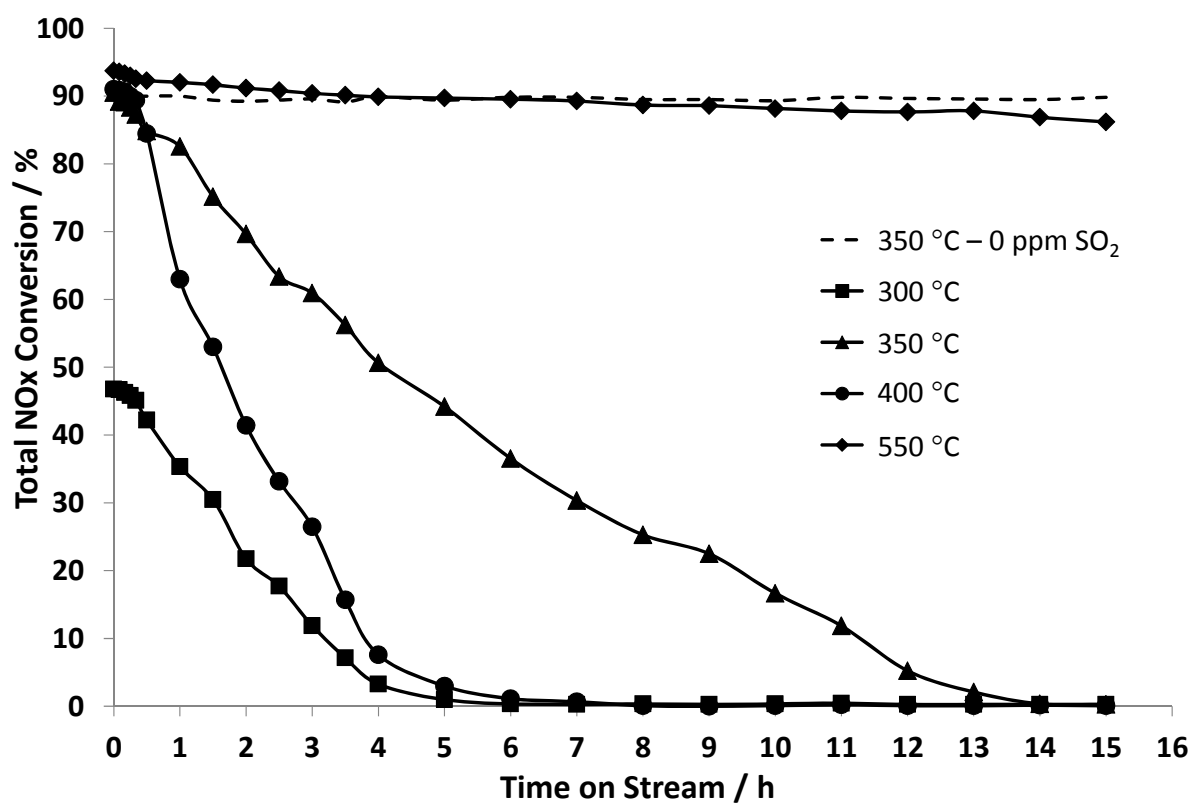


Figure 2 NO_x conversion as a function of time of exposure to the gas mix containing 5 ppm SO₂ (GM₂), at 300, 350, 400, and 550 °C. Feed conditions (GM₂): 720 ppm NO, 4340 C₈H₁₈ (as C1), 4.3% O₂, 7.2% CO₂, 7.2% H₂O, 5 ppm SO₂ and Ar balance.

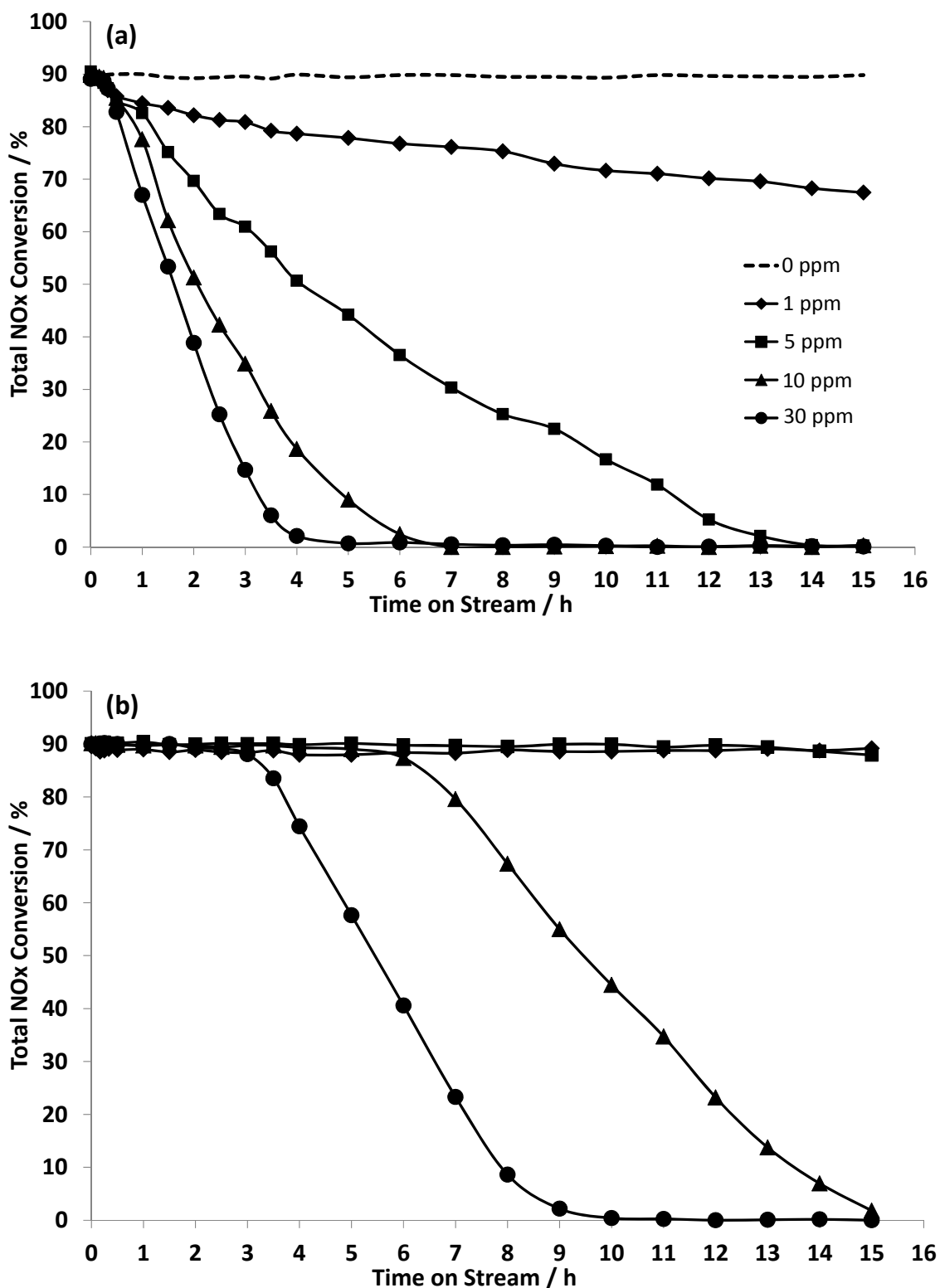


Figure 3 NO_x conversion as a function of time exposed to different concentrations of SO₂ (1-30 ppm) during octane-SCR of NO_x reaction at 350 °C over (a) single 2% Ag/Al₂O₃ and (b) 5% Ag/SiO₂ placed upstream of 2% Ag/Al₂O₃. Feed conditions (GM₂): 720 ppm NO, 4340 C₈H₁₈ (as C1), 4.3% O₂, 7.2% CO₂, 7.2% H₂O, 5 ppm SO₂ and Ar balance.

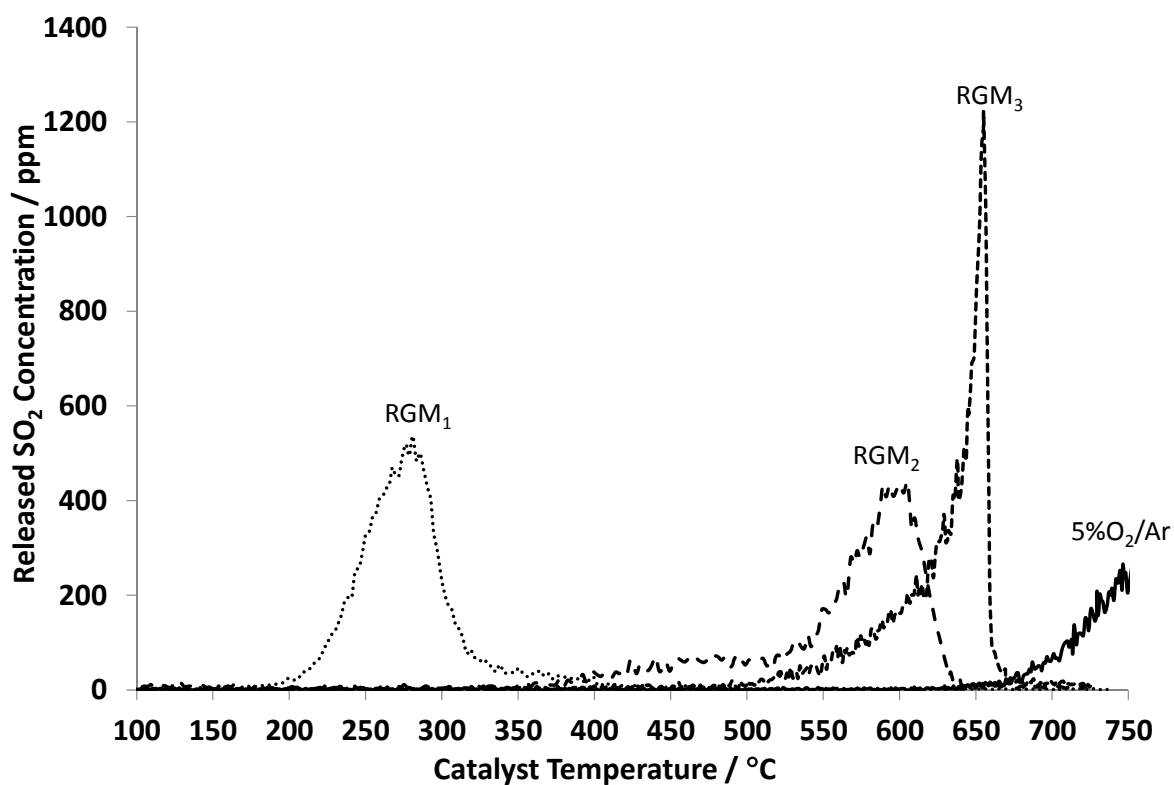


Figure 4 The profiles of desorbed SO₂ during temperature-programmed reactions using different regeneration mixes (RGM_x) without SO₂ over 5% Ag/SiO₂. Prior to these measurements, Ag/SiO₂ (276 mg) was exposed to GM₂ with 10 ppm SO₂ at 350 °C for 6 h.

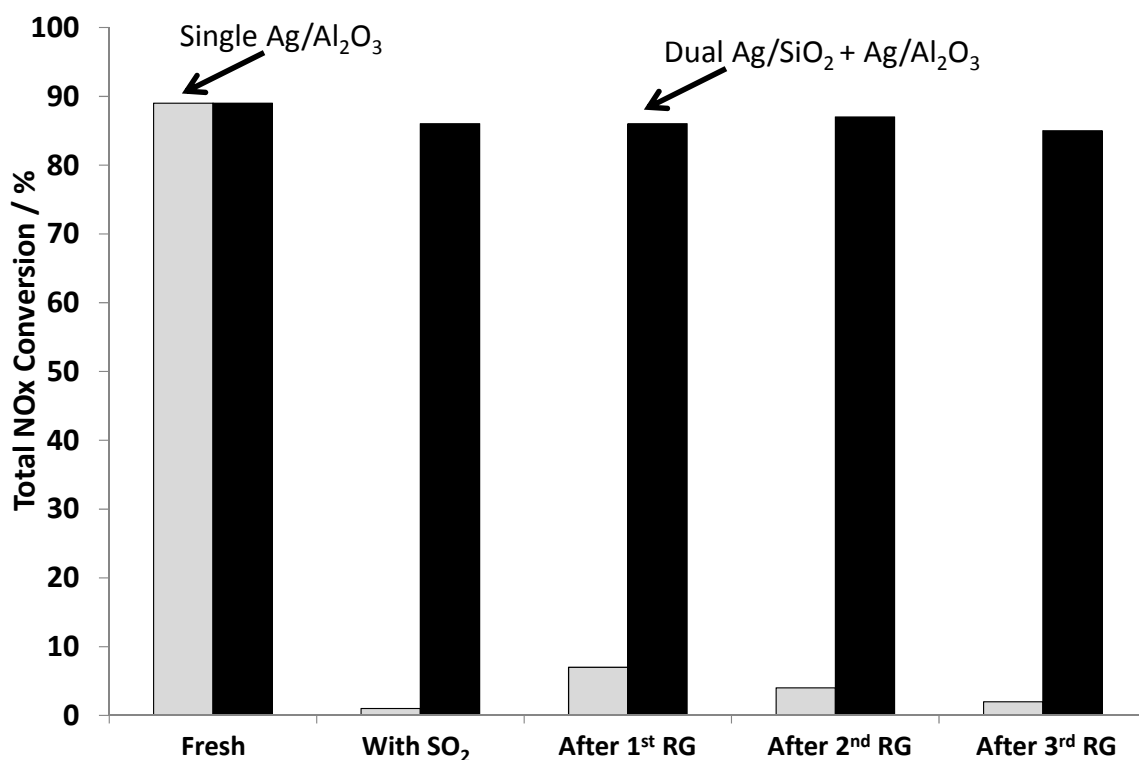


Figure 5 The effect of exposure to 5 ppm SO₂ at 350 °C and a 1 min regeneration time at 550 °C in rich conditions (RGM₁) containing 720 ppm NO, 542 ppm *n*-C₈H₁₈, 2% H₂, 5 ppm SO₂, 7.2% CO₂, 7.2% H₂O. All NO_x conversions were obtained at 350 °C after 15 h in gas mix GM₁ for fresh samples, and after 15 h under GM₂ (with SO₂ present) and then after 6 h under GM₂ after each regeneration step.

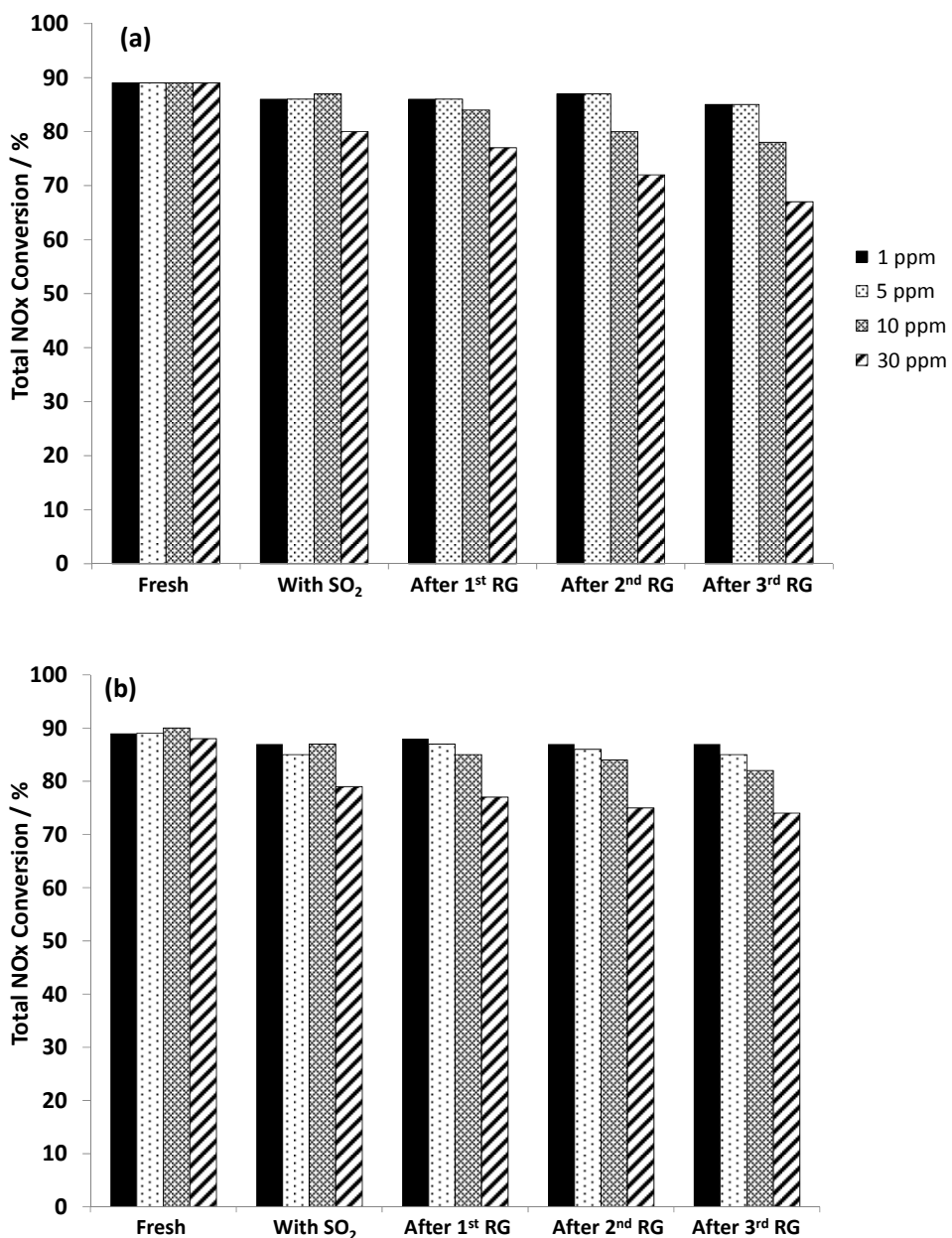


Figure 6 The effect of exposure to different concentration of SO₂ at 350 °C and (a) 1 min and (b) 5 min regeneration at 550 °C in rich conditions (RGM₁) containing 720 ppm NO, 542 ppm *n*-C₈H₁₈, 2% H₂, 5 ppm SO₂, 7.2% CO₂, 7.2% H₂O. All NO_x conversions were obtained at 350 °C at different times depending on the concentrations of added SO₂. Please refer to experimental section (Fig. 1) for details.

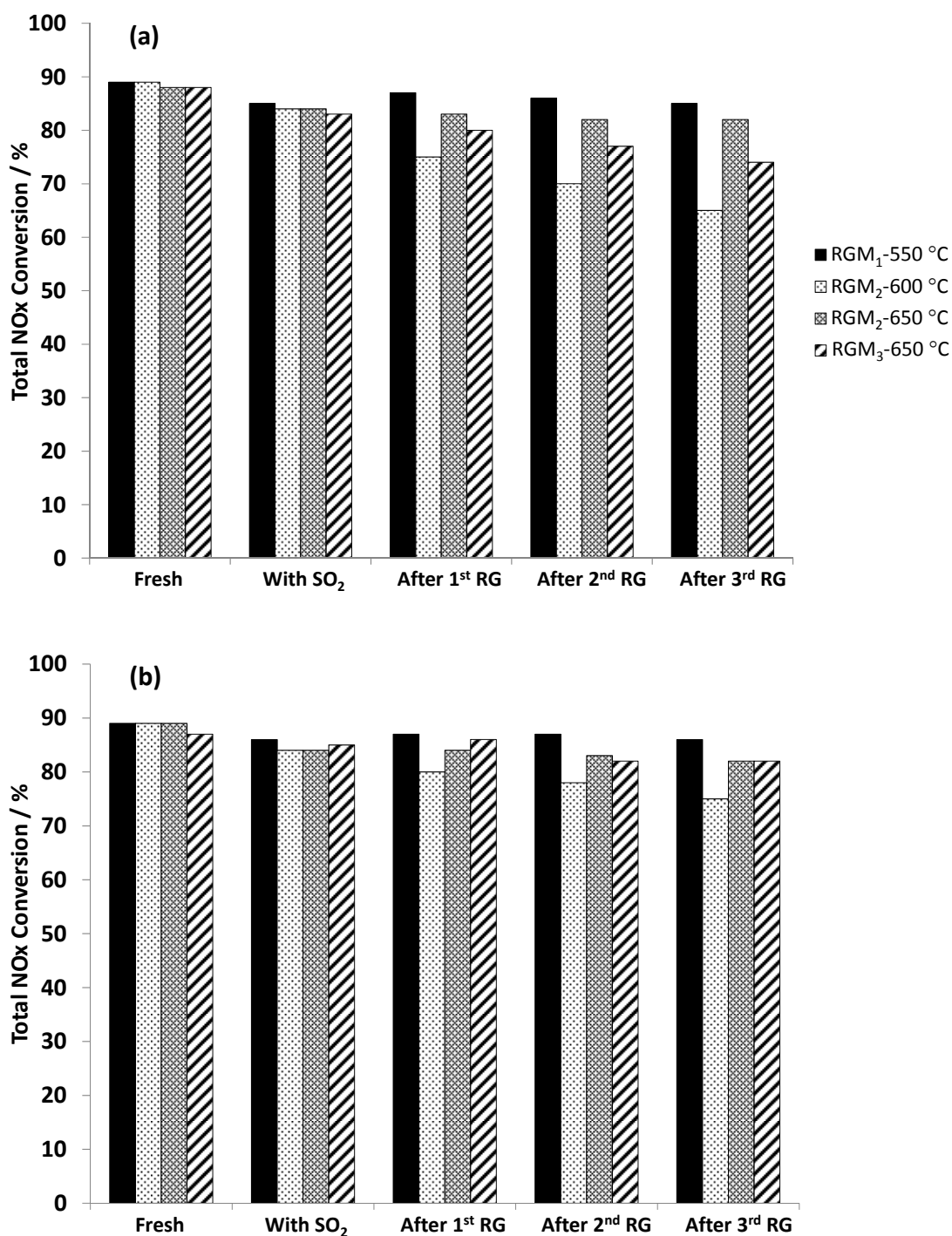


Figure 7 The effect of (a) 1 min and (b) 5 min regeneration using different mixes (RGM₁, RGM₂, and RGM₃) at 550, 600 or 650 °C. All NO_x conversions were obtained at 350 °C after 15 h in gas mix GM₁ for fresh samples, and after 15 h under GM₂ (with 5 ppm SO₂ present) and then after 6 h under GM₂ after each regeneration step. Please refer to the experimental section (Fig. 1) for details.